Chemical Equilibria

This chapter introduces straightforward equilibrium calculations. There isn't any complicated maths involved, although in some cases you will need to be able to do some very simple algebra. If your algebra is not very good, it's not a disaster!

Introduction – reminding you what the words mean

> ➤ **Note:** This is not a substitute for a standard text book. If you are unsure about any of the routine descriptive parts relating to equilibria, get them sorted out before you attack the calculations. All we are doing here is explaining a few key words which come up in numerical problems.

Dynamic homogeneous equilibrium

Homogeneous means that all the substances involved are in the same phase.

Phase is a better term than **physical state**. Phases are physically distinct parts of a system – parts that you can see boundaries between. If you had a solid and a gas, these are clearly two different parts of the total system and there is an obvious boundary between them. If, on the other hand, you had a mixture of gases, these would be a single phase because there would be no boundary.

The advantage of the term **phase** over physical state comes when you think of mixtures of liquids (or mixtures of solids). If you have two miscible liquids (for example, ethanol and water), these form a single phase with no boundary. But if you had two immiscible liquids (for example, petrol and water), one floats on top of the other with an obvious boundary between them. You would only have one physical state (liquid), but two phases.

A **dynamic equilibrium** involves a reversible reaction in a closed system – one from which nothing escapes (except heat) and to which nothing is added (except heat). For example, the Haber Process for the manufacture of ammonia involves the dynamic equilibrium:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
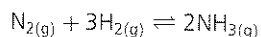
At equilibrium, the rate of the forward reaction (between nitrogen and hydrogen) becomes exactly equal to the rate of the back reaction (the splitting up of the ammonia).

So from then on there is no further change in the total amounts of nitrogen, hydrogen or ammonia present, because the ammonia is being formed at exactly the same rate as it is splitting up. There will only be a change in amounts if one of the conditions of the reaction (like temperature or pressure) is changed.

Dynamic implies that the reaction is still continuing. **Equilibrium** implies the constant amounts of everything.

Dynamic heterogeneous equilibrium

In this case a dynamic equilibrium exists where the substances are not all in the same phase. Typical examples include cases where mixtures of solids and gases are involved.

Dynamic homogeneous equilibria

The equilibrium constant, K_c

You will become familiar with two equilibrium constants, K_c and K_p. K_c is a constant derived from the concentrations of things present – which may be gases or liquids. K_p is derived from pressures, and only applies to gases. For now, we are going to consider K_c – the equilibrium constant in terms of concentrations.

Writing an expression for K_c

Suppose you have a dynamic homogeneous equilibrium with the equation:

$$aA + bB \rightleftharpoons cC + dD$$
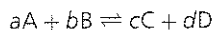
A, B, C and D are either all gases or all liquids – hence "homogeneous".

Suppose you allowed this reaction to reach equilibrium and then measured the steady concentrations of everything present. Irrespective of how much A or B or C or D you started with, you can write an expression involving them which always gives the same answer (provided you keep the temperature constant).

> ➤ From here on the word "dynamic" will be omitted. You can assume that any mention of the word "equilibrium" implies "dynamic equilibrium".

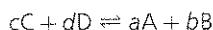That constant answer is called the **equilibrium constant** for the reaction and is given by the expression:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

[A], [B], [C] and [D] are simply the concentrations of the various substances in mol dm^{-3}.

> ➤ **Note!** Do not confuse the use of the powers in the equilibrium constant expression with the apparently similar use in the rate equations in Chapter 6. In the equilibrium constant expression, the powers are simply the numbers which appear in the equation. In the rate equations, the powers represent the orders of reaction, which can only be found from experiment, and which do not necessarily bear any relation to the numbers in the equation.

The powers (a, b, c and d) are the numbers which appear in front of the substances in the equation. If there isn't a number, the power is 1 – and the concentration term would just be written as, for example, [A].

> *Notice that equilibrium constants are always expressed by writing the right hand side terms on top and the left hand side terms underneath.*

You must write down the equation for the reaction to which the equilibrium constant applies, otherwise you cannot see which is the right hand side and which the left hand side. You could, for example, write the above reaction the other way around. That's fair enough – it's a reversible reaction, and you could just as well have produced an equilibrium mixture by starting from C and D:

$$cC + dD \rightleftharpoons aA + bB$$

The equilibrium constant for this reaction is

$$K_c = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

> ➤ If you look carefully at the two K_c expressions, you will see that the second one is simply the first one turned upside down. Suppose K_c for the reaction written one way is, say, 4. If the reaction was written the other way around, K_c would be 1/4 (or 0.25).

Both equilibrium constant expressions are perfectly valid. Both match the equations that accompany them. In an exam, you will probably be asked to write an expression for K_c for a reaction given to you by the examiners – in which case there's no problem. The equation will be written on the exam paper.

If you have to write your own equation, take care to get it properly balanced. You cannot write a correct expression for K_c from an incorrect equation.

Equilibrium constants are constant (at a particular temperature)

Nothing changes the value of the equilibrium constant except a change in temperature. Changing the pressure or the concentration of something or adding a catalyst makes no difference to the equilibrium constant, but a change in temperature will give it a different value. Calculating the new value is beyond A level, but you should be able to deduce whether it will increase or decrease. Use Le Chatelier's Principle to find out how the balance of the right hand side and left hand side of the equation changes.

e.g. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -92 \text{ kJ mol}^{-1}$
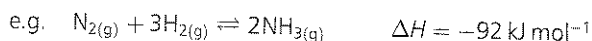
If you decrease the temperature, according to Le Chatelier the system will respond by favouring the reaction which will raise it again. It can do that by producing more ammonia because that reaction is exothermic. There will therefore be more ammonia and less nitrogen and hydrogen at equilibrium.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Because there will now be a bigger number on the top and smaller numbers on the bottom of the fraction, K_c will increase if you lower the temperature in this case.
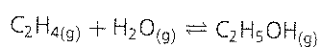
The units of K_c

The units of K_c vary from case to case, and you will have to work them out every time you calculate a value for K_c in a question. Write down the expression for K_c and then substitute units into it rather than numbers.
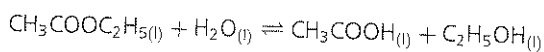
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
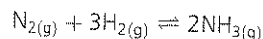
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^3}$$

$$= \frac{1}{(\text{mol dm}^{-3})^2}$$

$$= \frac{1}{\text{mol}^2 \text{ dm}^{-6}}$$

$$= \text{mol}^{-2} \text{ dm}^6$$

> ➤ **Hazy about Le Chatelier?** You shouldn't really be reading a chapter on equilibrium calculations if you haven't got the basic descriptive ideas properly under control. Stop now and do some revision.

> ➤ **Working out units:** If you are not familiar with how to work out units, stop now and read pages 129 to 130 in Chapter 6.

Example 1

Example 2

$$C_2H_{4(g)} + H_2O_{(g)} \rightleftharpoons C_2H_5OH_{(g)}$$

$$K_c = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]}$$

$$= \frac{mol\,dm^{-3}}{(mol\,dm^{-3})(mol\,dm^{-3})}$$

$$= \frac{1}{mol\,dm^{-3}}$$

$$= mol^{-1}\,dm^3$$

Example 3

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5][H_2O]}$$

$$= \frac{(mol\,dm^{-3})(mol\,dm^{-3})}{(mol\,dm^{-3})(mol\,dm^{-3})}$$

In this case, the units all cancel out and so K_c has no units – it is just a number. This will happen whenever there are exactly the same number of molecules on both sides of the equation. Look for this situation in examples – if you recognise it, you won't need to waste time working out non-existent units.
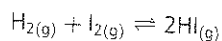
Problem . 1

Write down an expression for K_c and work out its units in each of the following examples:

(a) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
(b) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
(c) $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$
(d) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

Calculating values for K_c

Example 4

At its most trivial, all you might be asked to do is to write an expression for K_c and then substitute given values in it. This question relates to the equilibrium:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

When equilibrium had been established at 764 K, the mixture was found to contain: hydrogen $2.484 \times 10^{-3}\,mol\,dm^{-3}$; iodine $2.514 \times 10^{-3}\,mol\,dm^{-3}$; hydrogen iodide $1.695 \times 10^{-2}\,mol\,dm^{-3}$. Calculate a value for K_c at this temperature.

First write an expression for K_c:

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

➤ You might perhaps wonder why the concentrations of hydrogen and iodine are different. In fact, there isn't the slightest reason why they should be the same. They would only be the same if you mixed them initially in exactly the right proportions, or if you started from hydrogen iodide.

155

➤ **Note:** If there aren't any units, say so! It shows the examiners that you haven't just forgotten to work them out.

Example 5

➤ Dilute hydrochloric acid is often used as a convenient source of both water and acid catalyst. 18 g of dilute hydrochloric acid contains almost exactly 1 mole of water.

Then substitute the given values:

$$K_c = \frac{(1.695 \times 10^{-2})^2}{(2.484 \times 10^{-3})(2.514 \times 10^{-3})}$$

$$= 46.0 \text{ (no units)}$$

There are no units in this case, because there are the same number of molecules on both sides of the equation.

Most questions will need a bit more effort than the last one. This example is more typical.

If an ester like ethyl ethanoate reacts with water in the presence of an acid catalyst, the following equilibrium is established:

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$
ethyl ethanoate   ethanoic acid   ethanol
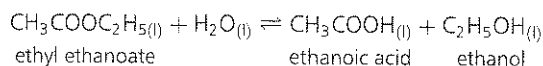
Exactly 1 mole of ethyl ethanoate was mixed with exactly 1 mole of water (from dilute hydrochloric acid) and allowed to reach equilibrium. The equilibrium mixture was analysed and found to contain 0.300 moles of ethanoic acid. Calculate a value for K_c at the temperature of the reaction.

To work out a value for K_c, you need to know the concentrations of everything at equilibrium. To find the concentrations, you need to know the number of moles of everything and the total volume. Draw up a little table to make clear what we actually know at the moment.

	$CH_3COOC_2H_{5(l)}$ +	$H_2O_{(l)}$ $\rightleftharpoons$	$CH_3COOH_{(l)}$ +	$C_2H_5OH_{(l)}$
Start (moles)	1	1	0	0
Equilibrium (moles)	?	?	0.300	?

You would not write the question marks down. These represent blanks that we need to think about before we put real values in.

Look at the relationships shown by the equation. Focus on one particular pair of substances at a time, and ignore everything else. Start with the ethanoic acid and the ethanol (because this is the easiest to see!).

The equation says that for every mole of ethanoic acid that is produced, you will also get one mole of ethanol. If 0.300 mole of ethanoic acid is formed, there will also be 0.300 mole of ethanol. You can slot that number into your table.

Now forget entirely about that relationship, and focus instead on the relationship between the ethanoic acid and the ethyl ethanoate. The equation says that 1 mole of ethyl ethanoate will react to produce 1 mole of ethanoic acid. Since 0.300 mole of ethanoic acid has been formed, 0.300 mole of ethyl ethanoate must have reacted. That leaves 0.700 mole. Slot that number into the table.

Now focus on the relationship between ethanoic acid and water. 1 mole of water reacts to produce 1 mole of ethanoic acid. 0.300 mole of water must have reacted, leaving 0.700 mole.

Your table now looks like this:

	$CH_3COOC_2H_{5(l)}$	+	$H_2O_{(l)}$	⇌	$CH_3COOH_{(l)}$	+ $C_2H_5OH_{(l)}$
Start (moles)	1		1		0	0
Equilibrium (moles)	1 − 0.300 = 0.700		1 − 0.300 = 0.700		0.300	0.300

Now we have a bit of a problem. In order to feed numbers into the equilibrium constant expression we need **concentrations** (in $mol\,dm^{-3}$), not numbers of moles. We are not told the volume of the mixture, and can't possibly guess it. Certainly we cannot assume that it will be $1\,dm^3$. We can't just ignore it either! So for now, call it "V", and hope something turns up later. The total calculation now looks like this:

	$CH_3COOC_2H_{5(l)}$	+	$H_2O_{(l)}$	⇌	$CH_3COOH_{(l)}$	+ $C_2H_5OH_{(l)}$
Start (moles)	1		1		0	0
Equilibrium (moles)	1 − 0.300 = 0.700		1 − 0.300 = 0.700		0.300	0.300
Equilibrium concentrations ($mol\,dm^{-3}$)	0.700/V		0.700/V		0.300/V	0.300/V

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5][H_2O]}$$

$$= \frac{(0.300/V)(0.300/V)}{(0.700/V)(0.700/V)}$$

$$= \frac{0.300 \times 0.300}{0.700 \times 0.700}$$

$$= 0.184 \text{ (no units)}$$

Conveniently, all the "V" terms cancel out. This happens because there are the same number of molecules on both sides of the equation. If there were different numbers of molecules on the right hand side and the left hand side, the volumes would not cancel. How would you cope with that problem? There would not be a problem, because the examiners would have to tell you the volume of the system in the question.

So was there any point in writing all the "V"s into the calculation if they were only going to cancel out again? YES! You must get into the habit of putting them in **every time**. Otherwise you are going to forget to do it when it really matters.

Example 6

This problem relates to the gaseous equilibrium:

$$B_{(g)} + C_{(g)} \rightleftharpoons A_{(g)}$$
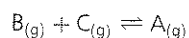
0.500 mole of B and 0.300 mole of C were mixed in a container of volume $10.0\,dm^3$ at a temperature of 400 K. At equilibrium there was found to be 0.100 mole of A present. Calculate the value for K_c at this temperature.

Example 7

|	$B_{(g)}$	+	$C_{(g)}$	$\rightleftharpoons$	$A_{(g)}$
Start (moles)	0.500		0.300		0
Equilibrium (moles)	0.500 − 0.100 = 0.400		0.300 − 0.100 = 0.200		0.100
Equilibrium concentration (mol dm⁻³)	0.400/10.0 = 0.0400		0.200/10.0 = 0.0200		0.100/10.0 = 0.0100

$$K_c = \frac{[A]}{[B][C]}$$

$$= \frac{0.0100}{0.0400 \times 0.0200}$$

$$= 12.5 \, \text{mol}^{-1} \, \text{dm}^3$$

So far, working out the "equilibrium (moles)" line has been straightforward because all the relationships involved in the equations have been 1:1. Where they are different (1:2, for example), there is more chance of making mistakes. This example illustrates the thinking involved.

The question refers to the gaseous equilibrium:
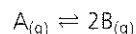
$$A_{(g)} \rightleftharpoons 2B_{(g)}$$

4.00 moles of A was placed in a 20.0 dm³ container and heated to 320 K until equilibrium had been established. The equilibrium mixture was found to contain 1.50 moles of A. Calculate the value for K_c at this temperature.

	$A_{(g)}$	$\rightleftharpoons$	$2B_{(g)}$
Start (moles)	4.00		0
Equilibrium (moles)	1.50		?

Thinking

2.50 moles of A has been used up (4.00 − 1.50).
Each mole of A used up produces two moles of B.
So at equilibrium there must be 2 × 2.50 moles of B present.

So the complete answer looks like this:

	$A_{(g)}$	$\rightleftharpoons$	$2B_{(g)}$
Start (moles)	4.00		0
Equilibrium (moles)	1.50		2 × (4.00 − 1.50) = 5.00
Equilibrium concentration (mol dm⁻³)	1.50/20.0 = 0.0750		5.00/20.0 = 0.250

$$K_c = \frac{[B]^2}{[A]}$$

$$= \frac{(0.250)^2}{0.0750}$$

$$= 0.833 \, \text{mol} \, \text{dm}^{-3}$$

Example 8

> **Remember:**
> Number of moles
> $$= \frac{\text{mass (g)}}{\text{mass of 1 mole (g)}}$$

> **Start** by working out how much ethanoic acid has been used up. This will be the same as the amount of ethyl ethanoate formed because of the 1:1 relationship between them in the equation.
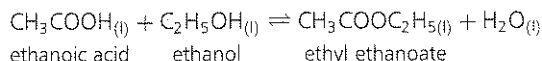>
> The amount of water formed will be the same as the amount of ethyl ethanoate formed, because they are also in a 1:1 relationship.
>
> The amount of ethanol used up will be the same as the amount of ethanoic acid used up – again a 1:1 relationship.
>
> We do not know what the volume of the original mixture is. It was **not** 250 cm³ – that was after you diluted it so that it could be titrated. The "V"s eventually cancel out.

Making life more difficult!

If you were going to work out an equilibrium constant from a real experiment, you would necessarily have to do more calculations than we have been doing. You would have to work out how many moles of starting substances you had, and find out how many moles of something you had at equilibrium. You could be asked to do the same thing in an exam – probably with some guidance.

24.0 g of ethanoic acid and 23.0 g of ethanol were mixed in a stoppered bottle and left for several days to reach equilibrium at room temperature. At the end of that time, the mixture was poured into pure water and made up to a total volume of 250 cm³. A 25.0 cm³ sample of this needed 26.5 cm³ of 0.400 mol dm⁻³ sodium hydroxide solution to neutralise the remaining ethanoic acid. Calculate a value for K_c for the reaction:

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$
ethanoic acid   ethanol   ethyl ethanoate

(H = 1; C = 12; O = 16. The equation for the reaction between ethanoic acid and sodium hydroxide is:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O)$$
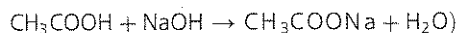
Finding the starting numbers of moles of ethanoic acid and ethanol is straightforward:

Number of moles of ethanoic acid $= 24.0/60 = 0.400$ moles

(1 mole weighs 60 g)

Number of moles of ethanol $= 23.0/46 = 0.500$ moles

(1 mole weighs 46 g)

Now you have to use the titration results to work out the number of moles of ethanoic acid at equilibrium. Start with what you know everything about – the sodium hydroxide.

$$\text{Number of moles of NaOH} = \frac{26.5}{1000} \times 0.400$$

$$= 0.0106$$

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

1 mole of NaOH reacts with 1 mole of ethanoic acid.

Therefore there are 0.0106 moles of ethanoic acid in the 25 cm³ sample.

In the whole 250 cm³ of solution there were 10×0.0106 moles of ethanoic acid $= 0.106$ moles.

This solution contained all of the equilibrium mixture. The equilibrium mixture therefore contained 0.106 moles of ethanoic acid.

Now we are back to the K_c calculations that we have been practising:

	$CH_3COOH_{(l)} + C_2H_5OH_{(l)}$		$\rightleftharpoons$ $CH_3COOC_2H_{5(l)}$	+ $H_2O_{(l)}$
Start (moles)	0.400	0.500	0	0
Equilibrium (moles)	0.106	0.500 − 0.294 = 0.206	0.400 − 0.106 = 0.294	0.294
Equilibrium concentration (mol dm⁻³)	0.106/V	0.206/V	0.294/V	0.294/V

159

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{(0.294/V)(0.294/V)}{(0.106/V)(0.206/V)}$$

$$= \frac{0.294 \times 0.294}{0.106 \times 0.206}$$

$$= 3.96 \text{ (no units)}$$

> ➤ There are no units because there are equal numbers of molecules on each side of the equation.

Problem • 2

This question relates to the reaction:

$$2M_{(g)} \rightleftharpoons N_{(g)}$$
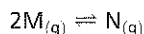
At equilibrium, the concentrations of M and N were respectively 0.141 mol dm⁻³ and 0.872 mol dm⁻³. Calculate the value for K_c at the temperature of the reaction.

Problem • 3

On heating, X decomposes reversibly according to the equation:

$$X_{(g)} \rightleftharpoons Y_{(g)} + Z_{(g)}$$

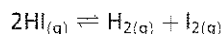This reaction was allowed to reach equilibrium at two different temperatures.

(a) When 1.00 mole of X was heated at 200 °C in a container of volume 25.0 dm³, the equilibrium mixture was found to contain 0.200 mole of Y. Calculate the value of K_c at this temperature.
(b) When the equilibrium constant was measured at 500 °C, K_c was found to have a value of 4.00×10^{-3} mol dm⁻³. Is the decomposition of X exothermic or endothermic? Explain your answer.

Problem • 4

A mixture of 2.00 mole of A and 1.00 mole of B was allowed to reach equilibrium according to the equation:

$$A_{(l)} + B_{(l)} \rightleftharpoons C_{(l)} + D_{(l)}$$
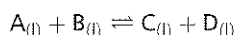
The equilibrium mixture was found to contain 0.400 mole of B. Calculate the value for K_c at the temperature of the reaction.

Problem • 5

1.00 mole of hydrogen iodide was heated in a container of volume 20.0 dm³ at a temperature of 765 K. At equilibrium, the mixture was found to contain 0.114 mole of iodine. Calculate K_c at this temperature for the equilibrium:

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Problem • 6

A mixture of 1.00 mole of ethanoic acid, 2.00 moles of ethanol and 1.00 mole of water was allowed to reach equilibrium. On analysis, the equilibrium mixture was found to contain 0.257 mole of ethanoic acid. Find K_c for the reaction:
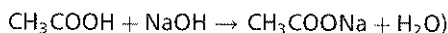
$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$
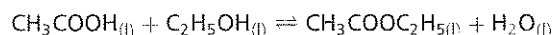
Problem . 7

44.0 g of ethyl ethanoate was mixed with 36.0 g of water containing hydrochloric acid as a catalyst and allowed to reach equilibrium over several days. The equilibrium mixture was then made up to 250 cm³ with pure water. A 25.0 cm³ sample of the diluted mixture was titrated with 1.00 mol dm⁻³ sodium hydroxide solution. After allowing for the acid catalyst present, the ethanoic acid in the equilibrium mixture was found to require 29.5 cm³ of the sodium hydroxide solution for neutralisation. Find K_c for the reaction:
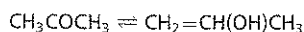
$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$
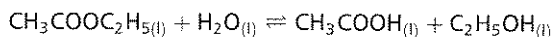
(H = 1; C = 12; O = 16. The equation for the neutralisation reaction is:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O)$$

Calculating things from given values of K_c

Although you have got to think carefully – especially at the "equilibrium (moles)" stage – there isn't any difficult maths in the calculations we have done so far. Reversing the calculations to find equilibrium concentrations from given values of K_c makes them more awkward, involving some algebra. In all but the very simplest cases, the algebra needed is beyond the demands of modern A level chemistry syllabuses. If you aren't very comfortable with algebra, it doesn't matter much – as you will see.
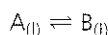
Example 9

> ➤ This could be described as an **isomerisation reaction**. Isomers are molecules with the same molecular formula but with a different spatial arrangement of the atoms. An example might be
>
> $CH_3COCH_3 \rightleftharpoons CH_2=CH(OH)CH_3$
>
> Each molecule has the same molecular formula, C_3H_6O, but the atoms are arranged differently.

This example is about a simple equilibrium

$$A_{(l)} \rightleftharpoons B_{(l)}$$

If 1.00 mole of A was allowed to reach equilibrium, how many moles of B would be formed if K_c had a value of 0.0200 at the temperature of the reaction?

Start off in exactly the same way as before:

	$A_{(l)}$	$\rightleftharpoons$	$B_{(l)}$
Start (moles)	1.00		0
Equilibrium (moles)	?		?

Now you have a problem, because you have no information to feed into this line. You are actually being asked to **find** the number of moles of B.

So write it in as an unknown. Call it "x" – or, perhaps rather more imaginatively, "b":

	$A_{(l)}$	$\rightleftharpoons$	$B_{(l)}$
Start (moles)	1.00		0
Equilibrium (moles)	?		b

If "b" moles of B have been formed, "b" moles of A have been used up because the relationship is 1:1. The number of moles of A left at equilibrium is therefore "$1.00 - b$".

161

	$A_{(l)}$	$\rightleftharpoons$	$B_{(l)}$
Start (moles)	1.00		0
Equilibrium (moles)	$1.00 - b$		b
Equilibrium concentration (mol dm^{-3})	$(1.00 - b)/V$		b/V

$$K_c = \frac{[B]}{[A]}$$

$$0.0200 = \frac{b/V}{(1.00 - b)/V}$$

$$0.0200 = \frac{b}{(1.00 - b)}$$

This is where the chemistry ends! Now you've got some algebra to do to solve this for "b":

$$0.0200 = \frac{b}{(1.00 - b)}$$

$$0.0200 \times (1.00 - b) = b$$

$$0.0200 - 0.0200b = b$$

$$1.02b = 0.0200$$

$$b = \frac{0.0200}{1.02}$$

$$= 0.0196 \, \text{mol}$$

Example 10 This example is very similar to the last one, except that the question is phrased differently.

The equilibrium $A_{(l)} \rightleftharpoons B_{(l)}$ has a value of K_c of 9 at a particular temperature. Calculate the fraction of the original A remaining when equilibrium is reached.

You are not told how much A to start with, but since you are asked about the **fraction** of it left over, you can start with any amount you choose.

It would make sense to start with 1 mole. If you calculated how many moles of A were left at equilibrium – say 0.25 of a mole – then 0.25 as a fraction of 1 is still 0.25. If you start with 1 mole and find the number of moles left over, you have automatically calculated the fraction left.

We'll call the fraction left "f".

	$A_{(l)}$	$\rightleftharpoons$	$B_{(l)}$
Start (moles)	1		0
Equilibrium (moles)	f		$1 - f$
Equilibrium concentration (mol dm^{-3})	f/V		$(1 - f)/V$

$$K_c = \frac{[B]}{[A]}$$

$$9 = \frac{(1-f)/V}{f/V}$$

$$9 = \frac{(1-f)}{f}$$

$$9f = 1 - f$$

$$10f = 1$$

$$f = \frac{1}{10} \quad (= 0.1 \text{ or } 10\%)$$

1/10 (or 0.1) of the A is left at equilibrium – or 10% if you are asked for a percentage.

Although most people would probably manage the algebra in the last two examples without too much difficulty, the problems mount up as soon as you have more than one molecule on either side of the equation.

Example 11   If K_c for the following reaction is 36 at a particular temperature, calculate the fraction of P converted into Q and R at equilibrium:
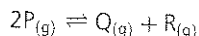
$$2P_{(g)} \rightleftharpoons Q_{(g)} + R_{(g)}$$

Again, you can start with however much P you like. Start with 1 mole, and call the fraction used up "f".

	$2P_{(g)}$	$\rightleftharpoons$	$Q_{(g)}$	+	$R_{(g)}$
Start (moles)	1		0		0
Equilibrium (moles)	$1-f$		$f/2$		$f/2$
Equilibrium concentrations (mol dm^{-3})	$(1-f)/V$		$(f/2)/V$ ($=0.5f/V$)		$(f/2)/V$ ($=0.5f/V$)

$$K_c = \frac{[Q][R]}{[P]^2}$$

$$36 = \frac{(0.5f/V) \times (0.5f/V)}{[(1-f)/V]^2}$$

$$36 = \frac{(0.5f) \times (0.5f)}{(1-f)^2}$$

Once you have got past the "equilibrium (moles)" line, all you are doing is substituting into the K_c expression. You will know by now that the "V"s always cancel as long as there are the same number of molecules on each side of the equation – so you ought to be able to get to this point in the calculation.

Unless your algebra is **good**, stop now! Don't waste time trying to solve it for "f". It is not likely to be worth many marks, it will take you ages, and you may well get it wrong anyway!

163

> The full solution of this problem is not given. If your algebra is good enough you will be able to do it yourself. If it isn't good enough, you shouldn't be wasting your time reading this!

There is a short cut to solving this particular equation. Notice that both sides of the equation are perfect squares. By taking the square root of both sides, you are left with:

$$\frac{0.5f}{(1-f)} = \pm 6$$

You now have to work out a value for "f" for each of the two possible roots, -6 and $+6$. You will find that the two possible answers are $f = 0.92$ and $f = 1.1$. Because "f" can't have a value greater than 1, the second answer is impossible. The fraction converted is 0.92.

Example 12

> **Read your syllabus.** If it says something like "Candidates will not be expected to solve quadratic equations" (possibly adding "... using the formula ...") then this example is not relevant to you.

> **Hint:** If "h" moles of H are formed, the same number of moles of G will be formed. If "h" moles of H are formed, that same number of moles of E and F will have been used up.

The equilibrium constant, K_c, for the following reaction is 4.0 at 20 °C.

$$E_{(l)} + F_{(l)} \rightleftharpoons G_{(l)} + H_{(l)}$$

If 2.0 moles of E and 1.0 mole of F were mixed and allowed to reach equilibrium at 20 °C, calculate the number of moles of H formed.

Call the amount of H formed "h".

	$E_{(l)}$	+	$F_{(l)}$	$\rightleftharpoons$	$G_{(l)}$	+	$H_{(l)}$
Start (moles)	2.0		1.0		0		0
Equilibrium (moles)	$2.0 - h$		$1.0 - h$		h		h
Equilibrium concentration ($mol\,dm^{-3}$)	$(2.0 - h)/V$		$(1.0 - h)/V$		h/V		h/V

$$K_c = \frac{[G][H]}{[E][F]}$$

$$4.0 = \frac{(h/V) \times (h/V)}{[(2.0 - h)/V] \times [(1.0 - h)/V]}$$

$$4.0 = \frac{h^2}{(2.0 - h) \times (1.0 - h)}$$

That's the chemistry finished! Even if your syllabus expects you to solve this, unless your algebra is **good**, stop there.

To solve this for "h", you need to rearrange the expression to give an equation of the form:

$$ax^2 + bx + c = 0$$

The solution of this is given by the expression:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Our equation rearranges to give:

$$3h^2 - 12h + 8 = 0$$

Solving this produces answers of 0.85 or 3.2, depending on whether you take the negative sign or positive sign in the expression above. You can't produce more than 1 mole of H because you are limited by the amount of F that you start with. The answer of 3.2 moles is therefore impossible, leaving you with the correct answer of 0.85 moles of H formed.

There isn't any difficult algebra in these questions apart from 10(b). You should only attempt that part if your syllabus expects you to solve quadratic equations.
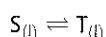
Problem . 8

The equilibrium constant for the reaction:

$$A_{(l)} \rightleftharpoons B_{(l)}$$
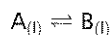
is 39 at 100 °C. If you had 2.0 moles of A to start with, how much would be left at equilibrium at this temperature?

Problem . 9

At 50 °C, K_c is 24 for the reaction:

$$S_{(l)} \rightleftharpoons T_{(l)}$$

What percentage of S will be converted into T when equilibrium is reached at this temperature?

Problem . 10

(a) In a closed system, the hydrolysis of ethyl ethanoate reaches equilibrium according to the equation:

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$

K_c has a value of 0.25 at room temperature. Suppose you started with 1 mole of ethyl ethanoate and set up a number of experiments with variable numbers ("w") of moles of water. Show that the fraction "f" of the ethyl ethanoate which reacts could be found by solving the equation:

$$\frac{f^2}{(1-f)(w-f)} = 0.25$$

(b) Find the fraction hydrolysed if $w = 1$ and if $w = 10$.

The equilibrium constant, K_p

Pressures and concentrations

Although many of the examples we have looked at involving K_c have related to gases, it is actually much easier to measure the pressure of a gas rather than its concentration. In fact, for a gas, concentration and pressure are proportional to each other. If you double the pressure for a fixed mass of gas at a constant temperature, you double the concentration. The reason is that the way you would double the pressure would be by halving the volume, and if you have the same amount of substance in half the volume, its concentration doubles.

You can also show this relationship mathematically if you are familiar with the ideal gas equation: $pV = nRT$. If you rearrange this you could produce the relationship:

$$p = \frac{n}{V} \times RT$$

n/V is just concentration – the number of moles divided by volume. As long as temperature is constant, RT is constant – and so pressure is proportional to concentration.

For gaseous equilibria it therefore makes sense to quote an equilibrium constant in terms of pressures rather than concentrations – i.e. K_p rather than K_c. There is a relationship between the two values, but you are unlikely to need it for A level purposes.

Before we can define K_p, we have to explain some other terms.

Mole fraction

This means literally what it says. If you have a mixture of gases (A, B, C, etc.) then the mole fraction of gas A is the fraction of the total number of moles which is gas A. The mole fraction of gas A is given the symbol x_A.

$$x_A = \frac{number\ of\ moles\ of\ gas\ A}{total\ number\ of\ moles\ of\ gas}$$

For example, if you had a mixture of 1 mole of oxygen and 4 moles of nitrogen, the total number of moles of gas is 5. The mole fraction of oxygen is therefore 1/5, and that of nitrogen 4/5.

It is important to realise that you could be given this information in an alternative way. For example, suppose you were told that you had a mixture of nitrogen and hydrogen which contained 25% by volume of nitrogen. Saying that the nitrogen makes up 25% of the volume is exactly the same as saying that the mole fraction of nitrogen is 25% (i.e. 0.25). The hydrogen, of course, makes up the rest of the volume, and its mole fraction would be 0.75.

> ➤ **Avogadro's Law** says that at the same temperature and pressure, equal volumes of gases contain equal numbers of molecules. 25% of the volume therefore means 25% of the total number of molecules. If you have 25% of the total number of molecules, you also have 25% of the total number of moles.

Partial pressure

The partial pressure of one of the gases in a mixture is the pressure which it would exert if it alone occupied the whole container. Partial pressure is given the symbol P_A or P_B (etc.).

Two important relationships

The total pressure is made up of the sum of the individual partial pressures:

$$Total\ pressure\ P = P_A + P_B + P_C + \ldots$$

$$Partial\ pressure\ of\ A = mole\ fraction\ of\ A \times total\ pressure$$
$$P_A = x_A \times P$$

Make sure you learn these – especially the second box. You can't do K_p calculations without them.
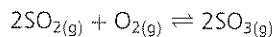
Writing an expression for K_p

Apart from the fact that partial pressures are used instead of concentrations, the equilibrium constant, K_p, is defined in exactly the same way as K_c. It is most easily seen using a couple of examples.

Example 13

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}$$

Notice that it is still "right hand side divided by left hand side".

Example 14

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
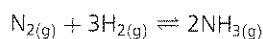
$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

Again, K_p is right hand side partial pressures divided by left hand side partial pressures, with everything raised to the power of whatever number is in front of it in the equation.

The units of K_p

Like K_c, K_p has units unless there are equal numbers of molecules on both sides of the equation. The sort of units will depend on what units for pressure the question uses – it could be pascals (Pa), or kilopascals (kPa), or megapascals (MPa), or even atmospheres (atm). It doesn't matter. Work with whatever you are given – and don't mess around with them! If you are given the units in kPa, stick to those units – don't waste time converting them into Pa.

Revisiting the two examples above:

Example 13a

Suppose you were given pressure units in kPa.

$$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}$$

$$= \frac{kPa^2}{kPa^2 \times kPa}$$

$$= \frac{1}{kPa}$$

$$= kPa^{-1}$$

Example 14a

Suppose you were given pressure units in atmospheres (atm).

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

$$= \frac{atm^2}{atm \times atm^3}$$

$$= \frac{1}{atm^2}$$

$$= atm^{-2}$$

> **Note!** Some books write brackets around the partial pressure terms – for example they write $(P_A)^2$ in the K_p expression. This is not a good idea! Without thinking very carefully, it is easy to write square brackets rather than round ones – in which case it looks as if you are confusing K_p and K_c. Since the brackets are totally unnecessary, leave them out.

Calculating values for K_p

Example 15

When A is heated in a closed system to $400\,^\circ$C, the following equilibrium is set up:

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$$
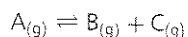
The equilibrium partial pressures of the three gases were found to be: A 5.1 kPa; B 95 kPa; C 95 kPa. Calculate K_p at this temperature.

You are given all the partial pressures, so all you need to do is slot them into the K_p expression:

$$K_p = \frac{P_B \times P_C}{P_A}$$

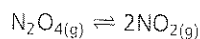$$= \frac{95 \times 95}{5.1}$$

$$= 1800\,\text{kPa}$$

> K_p has **units** in this case of
> $$\frac{(\text{kPa})^2}{\text{kPa}} = \text{kPa}$$

> **Significant figures?** No more than 2, because your input numbers are only to that accuracy.

Example 16

This refers to the equilibrium

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

A vessel containing only dinitrogen tetroxide was held at a temperature of 350 K until equilibrium was established. The equilibrium pressure was 123 kPa and the mole fraction of nitrogen dioxide was found to be 0.800. Calculate the value of K_p at this temperature.

Stop and think what you need to know. To find K_p, you need partial pressures. Are you given them? No! To find partial pressures, you need mole fractions. Are you given them? You are given the mole fraction of NO_2 but not of N_2O_4. You need to start by finding that.

If the mole fraction of NO_2 is 0.800, the mole fraction of N_2O_4 is $1 - 0.800$.

	N_2O_4	NO_2
Mole fractions	$1 - 0.800$ $= 0.200$	0.800
Partial pressures (kPa)	0.200×123 $= 24.6$	0.800×123 $= 98.4$

> **Remember:** partial pressure = mole fraction × total pressure

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
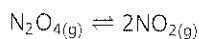
$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

$$= \frac{(98.4)^2}{24.6}$$

$$= 394\,\text{kPa}$$

> **Units** are exactly the same as in example 15.

Example 17

This example is about the Haber Process, where the equilibrium is:
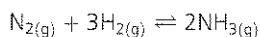
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

A mixture of nitrogen and hydrogen in the mole ratio 1:3 (as required by the equation) was heated to 700 K and a pressure of 79 atmospheres in the presence of an iron catalyst. The equilibrium mixture was found to contain the following proportions of gases (by volume): N_2 21%; H_2 63%; NH_3 16%. Calculate the value for K_p at this temperature.

Do you know the partial pressures? No! Do you know the mole fractions? Yes, you do! Remember that percentages by volume are a direct measure of the mole fractions. If there is 21% by volume of nitrogen, then the mole fraction of nitrogen is 21% – usually expressed as 0.21.

	N_2	H_2	NH_3
Mole fractions	0.21	0.63	0.16
Partial pressures (atm)	0.21×79	0.63×79	0.16×79
	$= 16.6$	$= 49.8$	$= 12.6$

> **Remember:**
> partial pressure = mole fraction × total pressure

> There should be no more than 2 **significant figures** in the final answer (because the percentages and pressure are only quoted to 2 figures).

> **Units?**
> $$\frac{atm^2}{atm \times atm^3} = \frac{1}{atm^2} = atm^{-2}$$

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

$$= \frac{(12.6)^2}{16.6 \times (49.8)^3}$$

$$= 7.7 \times 10^{-5} \ atm^{-2}$$

Example 18

This example uses exactly the same reaction with exactly the same figures as the last one, but you are given fewer of them!

This example is still about the Haber Process where the equilibrium is:
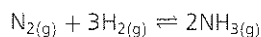
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

A mixture of nitrogen and hydrogen in the mole ratio 1:3 (as required by the equation) was heated to 700 K and a pressure of 79 atmospheres in the presence of an iron catalyst. The equilibrium mixture was found to contain 16% of ammonia by volume. Calculate the value for K_p at this temperature.

How do you get around the problem that you aren't told the mole fractions of nitrogen and hydrogen? If there is 16% ammonia in the equilibrium mixture, the rest must be nitrogen and hydrogen – 84%.

The nitrogen and hydrogen were in the mole ratio 1:3 at the start, and will remain in that same ratio throughout, because that is the ratio in which they are being used up.
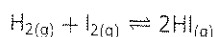
Of every 4 moles of nitrogen/hydrogen mixture, 1 will be nitrogen (1/4 of the total) and 3 will be hydrogen (3/4 of the total).

The nitrogen is therefore 1/4 of 84% (= 21%) and the hydrogen is 3/4 of 84% (= 63%). Now the rest of the calculation is exactly the same as before.

Example 19

Hydrogen and iodine were heated in a closed container at 1100 K until equilibrium was reached:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

The equilibrium partial pressures were hydrogen 50 kPa; iodine 50 kPa; and the total equilibrium pressure was 350 kPa. Find K_p.

Do you know the partial pressures? Almost. You are given all but the hydrogen iodide value. Remember that the total pressure is the sum of the partial pressures. We can account for 100 kPa of the total (50 + 50). The missing 250 kPa must be due to the hydrogen iodide.

> ➤ There aren't any **units**. There are equal numbers of molecules on both sides of the equation. If you did substitute units into the K_p expression, they would cancel out.

$$K_p = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$$

$$= \frac{(250)^2}{50 \times 50}$$

$$= 25 \text{ (no units)}$$

Example 20

When phosphorus(V) chloride is heated to a sufficiently high temperature it vaporises and dissociates according to the equation:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

> ➤ When a substance **dissociates**, it splits up (decomposes) reversibly.

When 1.00 mole of PCl_5 was heated in a closed container, the equilibrium pressure was found to be 100 kPa, and the equilibrium mixture contained 0.816 mole of chlorine. Calculate K_p at the temperature of the reaction.

Think about what you need to know. Do you know the partial pressures? No! Do you know the mole fractions? No! What do you need to know in order to find the mole fractions? You need the number of moles of each substance at equilibrium, and the total number of moles at equilibrium. You are given the equilibrium number of moles of chlorine – so the first thing to do is to calculate the number of moles of PCl_5 and PCl_3 at equilibrium. Until you know those, it is not possible to work out the total number of moles at equilibrium.

> ➤ Once a calculation starts to get as long as this one will turn out to be, you are likely to be given considerable guidance through it on a structured exam paper. The working here assumes that you have to think the whole thing out for yourself!

At this point you are back to the sort of simple problem that you met in K_c calculations.

	$PCl_{5(g)}$	$\rightleftharpoons$ $PCl_{3(g)}$	+ $Cl_{2(g)}$
Start (moles)	1	0	0
Equilibrium (moles)	?	?	0.816

If 0.816 mole of chlorine are formed, there must be the same amount of PCl_3. 0.816 mole of PCl_5 must have split up.

> ➤ **Note!** You must think carefully about the way this problem develops. It starts off looking like a K_c calculation, but changes direction after a couple of lines. It would be easy to get the two confused if you weren't careful. If the examiners are guiding you through the question, this difficulty doesn't arise, of course.

	$PCl_{5(g)}$	$\rightleftharpoons$ $PCl_{3(g)}$	+ $Cl_{2(g)}$
Equilibrium (moles)	1 − 0.816	0.816	0.816
	= 0.184		

This is our basic information. Now we can work out the total number of moles at equilibrium, because this is needed to find the mole fractions.

Total number of moles at equilibrium = 0.184 + 0.816 + 0.816

$$= 1.816$$

Now find the mole fractions and we are back on familiar territory. Remember that the total equilibrium pressure is 100 kPa.

|	PCl_5	PCl_3	Cl_2
Mole fractions	0.184/1.816 = 0.1013	0.816/1.816 = 0.4493	0.816/1.816 = 0.4493
Partial pressures (kPa)	0.1013 × 100 = 10.13	0.4493 × 100 = 44.93	0.4493 × 100 = 44.93

> **Remember:**
> partial pressure = mole fraction × total pressure

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

$$= \frac{44.93 \times 44.93}{10.13}$$

$$= 199 \text{ kPa}$$

Example 21

This example is very similar to the last one, but is slightly trickier at the "equilibrium (moles)" stage. It relates to the equilibrium:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$
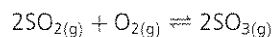
2.00 moles of sulphur dioxide and 1.00 mole of oxygen were mixed in the presence of a vanadium(V) oxide catalyst at a temperature of 700 K and an equilibrium pressure of 7.84 atmospheres. At equilibrium there were found to be 1.96 moles of sulphur trioxide in the mixture. Calculate K_p at this temperature.

Once again, think through what you need to know so that you can find the starting point for the calculation. Are you given partial pressures? No! Mole fractions? No! So you need to calculate the mole fractions – in which case you have to start by finding the numbers of moles of everything at equilibrium.

Try doing this before you read on.

	$2SO_{2(g)} +$	$O_{2(g)} \rightleftharpoons$	$2SO_{3(g)}$
Start (moles)	2.00	1.00	0
Equilibrium (moles)	?	?	1.96

The amount of SO_3 formed is exactly the same as the amount of SO_2 used up because their ratio in the equation is 1:1 (2:2 if you want to be fussy!).

Focusing on the relationship between the SO_3 and the oxygen, you will see that the amount of oxygen used up is only half the amount of SO_3 formed. Only half of 1.96 moles of oxygen have been used.

	$2SO_{2(g)} +$	$O_{2(g)} \rightleftharpoons$	$2SO_{3(g)}$
Equilibrium (moles)	2.00 − 1.96 = 0.04	1.00 − 1.96/2 = 0.02	1.96

The total number of moles present at equilibrium
$$= 0.04 + 0.02 + 1.96$$
$$= 2.02$$

171

	SO_2	O_2	SO_3
Mole fractions	0.04/2.02 = 0.01980	0.02/2.02 = 9.901×10^{-3}	1.96/2.02 = 0.9703
Partial pressures (atm)	0.01980×7.84 = 0.1552	$9.901 \times 10^{-3} \times 7.84$ = 0.07762	0.9703×7.84 = 7.607

> **Remember:**
> partial pressure = mole fraction × total pressure

$$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}$$

$$= \frac{(7.607)^2}{(0.1552)^2 \times 0.07762}$$

$$= 31\,000\,\text{atm}^{-1}$$

Example 22

0.200 moles of dinitrogen tetroxide, N_2O_4, were allowed to reach equilibrium at 25 °C according to the equation:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
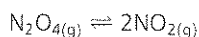
The equilibrium mixture contained 4.60 g of nitrogen dioxide and the equilibrium pressure was 0.431 atmospheres. Find K_p at 25 °C. (N = 14; O = 16).
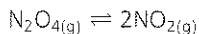
If you first find the number of moles of NO_2, the problem then becomes just like the last two. The RFM of NO_2 is 46.

4.60 g of NO_2 is 4.60/46 mol = 0.100 mol

	$N_2O_{4(g)}$	$\rightleftharpoons$	$2NO_{2(g)}$
Start (moles)	0.200		0
Equilibrium (moles)	0.200 − 0.100/2 = 0.150		0.100
The total number of moles	= 0.250		

> **Hint:** Each mole of NO_2 formed only needs half a mole of N_2O_4 to break up.

	N_2O_4	NO_2
Mole fractions	0.150/0.250 = 0.600	0.100/0.250 = 0.400
Partial pressures (atm)	0.600×0.431 = 0.2586	0.400×0.431 = 0.1724

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

$$= \frac{(0.1724)^2}{0.2586}$$

$$= 0.115\,\text{atm}$$

Problem . 11

When phosphorus(V) chloride reached equilibrium at 200 °C according to the equation:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$
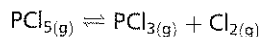
the equilibrium partial pressures were: PCl_5 40 kPa; PCl_3 80 kPa; Cl_2 80 kPa. Calculate K_p at this temperature.
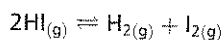
Problem . 12

N_2O_4 dissociates according to the equation:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
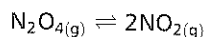
When equilibrium had been established at a temperature of 298 K and an equilibrium pressure of 101 kPa, the partial pressure of N_2O_4 was found to be 72.0 kPa. Calculate K_p at this temperature.

Problem . 13

When hydrogen iodide was heated in a closed container to a temperature of 700 K, the total pressure at equilibrium was 1.00 atmosphere, and the partial pressure of the hydrogen iodide was 0.786 atmosphere. Find K_p for the reaction:

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Problem . 14

1.00 mole of carbon monoxide and 1.00 mole of steam were allowed to reach equilibrium at 700 K and a pressure of 1.50 atmospheres. 0.740 mole of carbon dioxide was formed at equilibrium. Find K_p for the reaction:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$
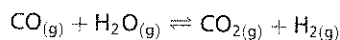
Problem . 15

640 g of sulphur dioxide were mixed with 256 g of oxygen and allowed to reach equilibrium in the presence of a vanadium(V) oxide catalyst at 700 K. The equilibrium pressure was 1.40 atmospheres and the mixture was found to contain 792 g of sulphur trioxide. Find the value of K_p for the equilibrium:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$
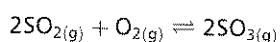
(O = 16; S = 32)

Calculating things from given values of K_p

The following examples all involve the same equilibrium at the same temperature (350 K):

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_p = 3.89\,atm$$
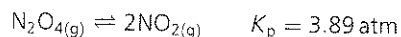
Example 23

When the above equilibrium was established at 350 K, the partial pressure of the NO_2 was found to be 0.700 atm. Calculate the partial pressure of the N_2O_4, and the total pressure.

Start by writing the expression for K_p, and then slot in the numbers you know:

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

$$3.89 = \frac{(0.700)^2}{P_{N_2O_4}}$$

$$P_{N_2O_4} = \frac{(0.700)^2}{3.89}$$

$$= 0.126\,\text{atm}$$

The total pressure is the sum of the partial pressures:

Total pressure $= 0.700 + 0.126$
$$= 0.826\,\text{atm}$$

Example 24

This is the same problem, but you are starting with the other partial pressure. It is possible to make a careless mistake this time.

When the above equilibrium was established at 350 K, the partial pressure of the N_2O_4 was found to be 0.200 atm. Calculate the partial pressure of the NO_2, and the total pressure.

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

$$3.89 = \frac{P^2_{NO_2}}{0.200}$$

$$P^2_{NO_2} = 0.200 \times 3.89$$

$$= 0.778$$

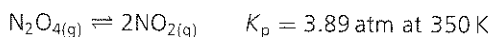$$P_{NO_2} = \sqrt{0.778}$$

$$= 0.882\,\text{atm}$$

Total pressure $= 0.200 + 0.882$
$$= 1.08\,\text{atm}$$

> ➤ It is easy to forget to take the square root in the last step.

Example 25

We are still talking about the same equilibrium:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_p = 3.89\,\text{atm at }350\,\text{K}$$

When 1.00 mole of dinitrogen tetroxide was heated to 350 K in a closed container, the equilibrium mixture was found to contain 0.600 mole of nitrogen dioxide. Calculate the total pressure at equilibrium, and the partial pressures of N_2O_4 and NO_2.

This is a much trickier question than the last one, and you would almost certainly be guided through it in an exam.

Work out the number of moles of dinitrogen tetroxide left at equilibrium.

> ➤ **Hint:** Each mole of NO_2 formed only needs half a mole of N_2O_4 to break up.

	$N_2O_{4(g)}$	$\rightleftharpoons$	$2NO_{2(g)}$
Start (moles)	1.00		0
Equilibrium (moles)	1.00 − 0.600/2 = 0.700		0.600

If the total pressure of the system at equilibrium is P, work out the partial pressures of N_2O_4 and NO_2 in terms of P.

The total number of moles at equilibrium is 1.300 (0.700 + 0.600).

	N_2O_4	NO_2
Mole fractions	0.700/1.300 = 0.5385	0.600/1.300 = 0.4615
Partial pressures (atm)	$0.5385 \times P$	$0.4615 \times P$

Write an expression for K_p and use it to calculate the total pressure P:

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

$$3.89 = \frac{(0.4615 \times P)^2}{0.5385 \times P}$$

$$3.89 = \frac{(0.4615)^2 \times P}{0.5385}$$

$$P = \frac{3.89 \times 0.5385}{(0.4615)^2}$$

$$= 9.84 \, atm$$

Calculate the partial pressures of N_2O_4 and NO_2.

All you have to do is to substitute P into the expressions in the bottom row of the table above:

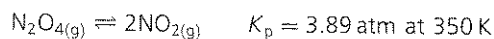Partial pressure of $N_2O_4 = 0.5385 \times 9.84$
$$= 5.30 \, atm$$

Partial pressure of $NO_2 = 0.4615 \times 9.84$
$$= 4.54 \, atm$$

Example 26

This problem involves doing some complicated algebra. You don't need to read it unless your syllabus expects you to solve quadratic equations.

Still the same equilibrium:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_p = 3.89 \, atm \, at \, 350 \, K$$

If dinitrogen tetroxide is allowed to reach equilibrium at a temperature of 350 K and an equilibrium pressure of 2.00 atmospheres, calculate the partial pressures of dinitrogen tetroxide and nitrogen dioxide in the mixture.

The first thing to notice is that you only need to calculate one of the partial pressures in the first instance. Suppose, for example, that we set out to find the partial pressure of the NO_2 – call it "p". Because the total pressure is the sum of the partial pressures, the partial pressure of N_2O_4 will be $2.00 - p$.

Write the K_p expression and then substitute into it:

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

$$3.89 = \frac{p^2}{(2.00 - p)}$$

175

> If your algebra is not good enough to cope with this, don't waste your time on it. Derive the expression involving p from K_p and leave it at that. You must, however, explain how you would obtain the partial pressure of N_2O_4. You could say something like 'If p worked out to be 0.500 atm, then the partial pressure of N_2O_4 would be $2.00 - 0.500 = 1.50$ atm.' It is obviously the wrong answer, but you should get credit for it.

Now there is some algebra to do:

$$3.89 \times (2.00 - p) = p^2$$

$$7.78 - 3.89p = p^2$$

$$p^2 + 3.89p - 7.78 = 0$$

Solve this using:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

You get two possible answers depending on whether you take the positive or negative sign. The solutions are 1.46 or -5.35. The negative answer is obviously impossible.

The partial pressure of NO_2 is 1.46 atm.

The partial pressure of N_2O_4 is $(2.00 - 1.46)$ atm $= 0.54$ atm.

Problem • 16

When hydrogen iodide is heated in a closed container, it reaches equilibrium according to the equation:

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)} \qquad K_p = 0.0185 \text{ at } 700\,K$$

If the partial pressure of hydrogen iodide in the mixture is 1.32 atmospheres, calculate the partial pressures of hydrogen and of iodine and the total equilibrium pressure. (Hint: The hydrogen and iodine are produced in equal amounts when the hydrogen iodide splits up.)

Problem • 17

If sulphur dioxide and oxygen are mixed in the presence of a vanadium(V) oxide catalyst, the following equilibrium can be established:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad K_p = 0.130 \text{ atm}^{-1} \text{ at } 1100\,K$$
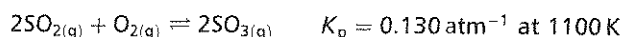
The sulphur dioxide and oxygen were mixed in the mole ratio 2:1 (as required by the equation) and heated to 1100 K. A 50.0% conversion of SO_2 into SO_3 was required.

(a) If you started with 2.00 moles of sulphur dioxide and 1.00 mole of oxygen, calculate the numbers of moles of everything present in the equilibrium mixture assuming 50.0% conversion.
(b) If the total equilibrium pressure is P, write expressions for the partial pressures of SO_2, O_2 and SO_3 in terms of P.
(c) Write an expression for K_p and use it to calculate the total pressure P.

Problem • 18

When some dinitrogen tetroxide was allowed to reach equilibrium at 298 K in a closed container, it was found that 20.0% of it had dissociated into nitrogen dioxide according to the equation:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_p = 0.115 \text{ atm at } 298\,K$$
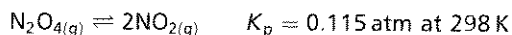
(a) Assuming that you started with 100 moles of N_2O_4, calculate the numbers of moles of N_2O_4 and NO_2 present at equilibrium.
(b) If the total equilibrium pressure is P, write expressions for the partial pressures of N_2O_4 and NO_2 in terms of P.
(c) Write an expression for K_p and use it to calculate the total pressure P.
(d) Work out the partial pressures of N_2O_4 and NO_2.

> **Note:** Don't attempt this question unless your syllabus expects you to be able to solve quadratic equations.

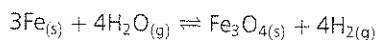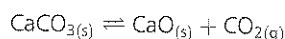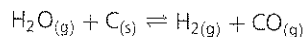When phosphorus(V) chloride is heated, the following equilibrium is established:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_p = 160\,kPa\ at\ 200\,°C$$

(a) If the partial pressure of chlorine at equilibrium is p, calculate the partial pressures of PCl_5 and PCl_3 at equilibrium in terms of p if the total pressure is 400 kPa.

(b) Write an expression for K_p, and use it to calculate a value for p.

(c) Work out the partial pressures of each component of the equilibrium mixture.
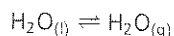
Dynamic heterogeneous equilibria

Examples of heterogeneous equilibria

> **Note!** Not all syllabuses expect you to know about heterogeneous equilibria. Check your syllabus, and if you are in any doubt, look at recent exam questions, or contact the Examination Board.

In a heterogeneous equilibrium, more than one phase is present. The most common examples involve gases in contact with solids, but you could also have gases in contact with liquids, or solids in contact with liquids.

Gases in contact with solids

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons H_{2(g)} + CO_{(g)}$$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$$

Gases in contact with liquids

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

This is the equilibrium which is established when you have some water in a closed bottle. Some of the water evaporates to give water vapour in the space above the liquid water.

Solids in contact with liquids

If you shook copper up with silver nitrate solution, you would get this equilibrium established:

$$Cu_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag_{(s)}$$
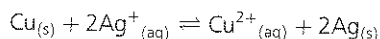
This is the sort of equilibrium which you get if you shake any sparingly soluble ionic substance with water:

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$
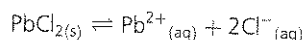
Equilibria like this second example are dealt with separately in Chapter 9 under "Solubility product". Check your syllabus to find out whether this is something you need to know about.

··

Equilibrium constants for heterogeneous equilibria

Important rule

> *When writing an expression for the equilibrium constant for a heterogeneous equilibrium, terms for pure solids or pure liquids are left out of the expression.*
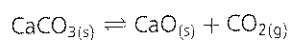
This applies whether you are writing an expression for K_c or K_p.

Example 27

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons H_{2(g)} + CO_{(g)}$$

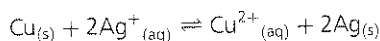| The correct expressions	NOT
$K_c = \dfrac{[H_2][CO]}{[H_2O]}$	$\dfrac{[H_2][CO]}{[H_2O][C]}$
$K_p = \dfrac{P_{H_2} \times P_{CO}}{P_{H_2O}}$	$\dfrac{P_{H_2} \times P_{CO}}{P_{H_2O} \times P_C}$

Example 28

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$K_c = [CO_2] \qquad K_p = P_{CO_2}$$

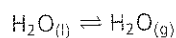Notice that neither of the solids is represented in the equilibrium expressions.

Example 29

> ➤ There is no K_p expression this time because the equilibrium doesn't involve gases.

$$Cu_{(s)} + 2Ag^+{}_{(aq)} \rightleftharpoons Cu^{2+}{}_{(aq)} + 2Ag_{(s)}$$

$$K_c = \dfrac{[Cu^{2+}]}{[Ag^+]^2}$$

Once again, neither solid is included in the K_c expression.

Example 30

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

$$K_p = P_{H_2O_{(g)}}$$

The liquid water is not included because it is a pure liquid phase.

Calculations involving heterogeneous equilibria

Once you know how to write expressions for the equilibrium constants, the calculations are identical to those for homogeneous equilibria. Here are two examples to illustrate this:

Example 31

When steam was heated with excess carbon to 1200 K and an equilibrium pressure of 15.5 atmospheres, 90.0% of the steam was converted into hydrogen and carbon monoxide. Calculate K_p for the equilibrium:

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons H_{2(g)} + CO_{(g)}$$
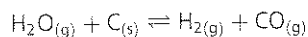
Since we are given information about percentage conversion, we will start with 100 moles of steam. If you wanted to, you could start with 1 mole, but you would then have to think slightly more (for example, to convert 90% into the decimal fraction 0.9)!

> ➤ We are not interested in the carbon as far as the equilibrium calculation is concerned, so we leave that space blank.

	$H_2O_{(g)}$	+	$C_{(s)}$	$\rightleftharpoons$	$H_{2(g)}$	+	$CO_{(g)}$
Start (moles)	100		—		0		0
Equilibrium (moles)	100 − 90.0 = 10.0		—		90.0		90.0

The total number of moles of gas at equilibrium is $10.0 + 90.0 + 90.0 = 190$.

	H_2O	H_2	CO
Mole fractions	10.0/190 = 0.05263	90.0/190 = 0.4737	90.0/190 = 0.4737
Partial pressures (atm)	0.05263 × 15.5 = 0.8158	0.4737 × 15.5 = 7.342	0.4737 × 15.5 = 7.342

> ➤ **Remember:**
> partial pressure = mole fraction × total pressure

$$K_p = \frac{P_{H_2} \times P_{CO}}{P_{H_2O}}$$

$$= \frac{7.432 \times 7.432}{0.8158}$$

$$= 67.7 \, atm$$

Example 32

Carbon monoxide was placed in a closed container with an excess of iron(II) oxide and heated to 1000 °C. The equilibrium pressure was 200 kPa. Calculate the partial pressures of carbon monoxide and carbon dioxide.

$$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)} \qquad K_p = 0.403$$
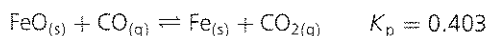
We don't need to worry about the iron(II) oxide or the iron, because they are both solids, and won't appear in the K_p expression.

If we work out one of the partial pressures, we can easily find the other one because the total pressure is the sum of the partial pressures.

Call the partial pressure of carbon monoxide "p". The partial pressure of the carbon dioxide will then be $(200 - p)$.

$$K_p = \frac{P_{CO_2}}{P_{CO}}$$

$$0.403 = \frac{(200 - p)}{p}$$

$$0.403p = 200 - p$$

$$1.403p = 200$$

$$p = 143 \, kPa$$

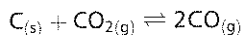The partial pressure of carbon monoxide is 143 kPa.

The partial pressure of carbon dioxide is $(200 - 143) \, kPa = 57 \, kPa$.

Problem • 20

When carbon is heated in the presence of carbon dioxide, the following equilibrium can be established:

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$$

At 850 °C and an equilibrium pressure of 5.00 atmospheres, the equilibrium mixture is found to contain 21.7% carbon dioxide and 78.3% carbon monoxide. Write an expression for K_p and calculate its value at this temperature.

Problem • 21

When a solution containing 1.0 mol dm^{-3} of Pb^{2+}$_{(aq)}$ ions is shaken with some finely divided tin, the following equilibrium is set up:

$$Sn_{(s)} + Pb^{2+}{}_{(aq)} \rightleftharpoons Pb_{(s)} + Sn^{2+}{}_{(aq)} \qquad K_c = 2.2 \text{ at } 25\,°C.$$
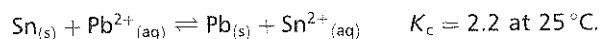
Calculate the fraction of the Pb^{2+}$_{(aq)}$ ions which is converted to solid lead.

Problem • 22

Steam was heated with an excess of carbon to 1000 K. What was the equilibrium pressure if the equilibrium mixture of gases contained 50% steam, 25% hydrogen and 25% carbon monoxide?

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons H_{2(g)} + CO_{(g)} \qquad K_p = 3.7 \text{ atm at } 1000\,K$$
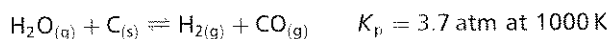
> ➤ You may not need to do all these things. Check your syllabus and past exam papers.

End of chapter checklist

Can you do the following things?

■ Write expressions for K_c and K_p for homogeneous reactions.

■ Know that for heterogeneous reactions, concentration or pressure terms for pure solid or pure liquid phases are omitted from the K_c or K_p expressions.

■ Write expressions for K_c and K_p for heterogeneous reactions.

■ Deduce the units for any given K_c or K_p expression.

■ Understand the terms mole fraction and partial pressure and state the relationship between them.

■ Calculate values for K_c or K_p given suitable data.

■ Use given values of K_p or K_c to calculate equilibrium concentrations or pressures.

Revision problems

Numerical answers are provided for these problems, but no worked solutions. None of these problems contain any difficult algebra.
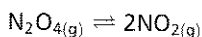
Problem • 23

For the equilibrium:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \quad \text{at } 700\,K$$
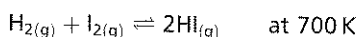
(a) Write an expression for K_c and calculate its value if the equilibrium concentrations are: H_2 0.214 mol dm^{-3}; I_2 0.214 mol dm^{-3}; HI 1.57 mol dm^{-3}.

(b) Write an expression for K_p and calculate its value if the equilibrium partial pressures are: H_2 0.642 kPa; I_2 0.642 kPa; HI 4.71 kPa.

Problem • 24

1.00 mol of N_2O_4 was warmed to 350 K in a container of volume 7.88 dm^3. At equilibrium, 40% of the N_2O_4 had converted into NO_2. The equilibrium pressure was 517 kPa.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

(a) Calculate the numbers of moles of N_2O_4 and NO_2 present at equilibrium.

(b) Write an expression for K_c and calculate its value.

(c) Work out the partial pressures of N_2O_4 and NO_2 at equilibrium.

(d) Write an expression for K_p and calculate its value.

Problem • 25

A Haber Process plant manufacturing ammonia operated at a pressure of 100 atmospheres and a temperature of 400 °C. When the nitrogen and hydrogen were mixed in the 1:3 ratio required by the equation, the equilibrium mixture was found to contain 25.2% of ammonia by volume.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
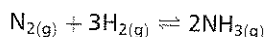
(a) Calculate the percentages of nitrogen and hydrogen in the equilibrium mixture.

(b) Calculate the partial pressures of nitrogen, hydrogen and ammonia at equilibrium.

(c) Write an expression for K_p and calculate its value at this temperature.

Problem • 26

41.7 g of phosphorus(V) chloride was heated to 200 °C in a container of volume 15.7 dm^3. When equilibrium was established, the mixture was found to contain 11.36 g of chlorine. The equilibrium pressure was found to be 90.0 kPa.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$
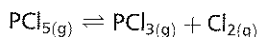
(a) Calculate the numbers of moles of PCl_5, PCl_3 and Cl_2 present at equilibrium. (P = 31; Cl = 35.5)

(b) Write an expression for K_c and calculate its value at this temperature.

(c) Work out the partial pressures of PCl_5, PCl_3 and Cl_2 at equilibrium.

(d) Write an expression for K_p and calculate its value.

181

Problem · 27

1.0 mol of ethanoic acid and 2.0 mol of ethanol were mixed and allowed to reach equilibrium:

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$
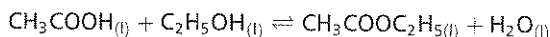
The equilibrium mixture was carefully diluted with pure water to a total volume of 250 cm³. A 25 cm³ sample of this required 15.5 cm³ of 1.00 mol dm⁻³ sodium hydroxide solution to neutralise the ethanoic acid present. Calculate K_c at the temperature of the reaction.
(The neutralisation reaction is:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O)$$
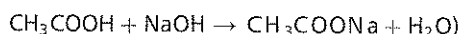
Problem · 28

When steam was heated with excess carbon in a closed container to 1800 kPa, the partial pressure of steam at equilibrium was 318 kPa:

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons H_{2(g)} + CO_{(g)}$$
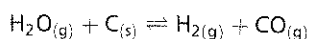
(a) Work out the partial pressures of hydrogen and carbon monoxide.
(b) Write an expression for K_p for the heterogeneous equilibrium, and calculate its value.
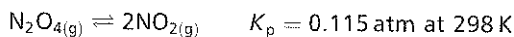
Problem · 29

Solid ammonium hydrogensulphide dissociates according to the equation:

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)} \qquad K_p = 0.109\,atm^2 \text{ at } 25\,°C$$
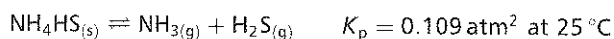
If ammonium hydrogensulphide dissociates in a closed container at 25 °C, calculate the equilibrium partial pressures of ammonia and hydrogen sulphide.
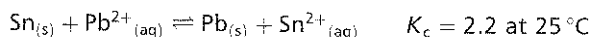
Problem · 30

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_p = 0.115\,atm \text{ at } 298\,K$$

If the equilibrium partial pressure of N_2O_4 is 0.500 atmosphere, calculate the equilibrium partial pressure of NO_2, and the total equilibrium pressure.

Problem · 31

An excess of finely divided tin and lead was shaken with a solution containing 1.0 mol dm⁻³ of lead(II) ions and 0.50 mol dm⁻³ of tin(II) ions. Calculate the equilibrium concentrations of lead(II) and tin(II) ions:

$$Sn_{(s)} + Pb^{2+}_{(aq)} \rightleftharpoons Pb_{(s)} + Sn^{2+}_{(aq)} \qquad K_c = 2.2 \text{ at } 25\,°C$$

Problem · 32

If solid PCl₅ is heated to 200 °C, it vaporises and dissociates according to the equation:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_p = 160\,kPa \text{ at } 200\,°C$$
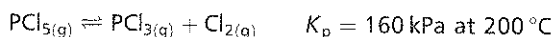
90.0% of the PCl₅ is found to have dissociated.

(a) If the total equilibrium pressure is P, write expressions for the partial pressures of the gases present at equilibrium in terms of P.
(b) Write an expression for K_p and use it to calculate the total pressure P.
(c) Calculate the partial pressures of the gases present at equilibrium.

Problem · 33

Steam was heated with carbon at 1100 K until equilibrium was established. 80% of the steam was converted into hydrogen and carbon monoxide:

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons H_{2(g)} + CO_{(g)} \qquad K_p = 17\,atm \text{ at } 1100\,K$$
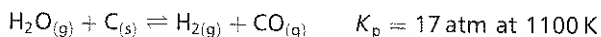
Calculate the total equilibrium pressure.